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Impact of Volcanic Eruptions on the Occurrence of PAHs Compounds in the Aquatic Ecosystem of the Southern Part of West Spitsbergen (Hornsund Fjord, Svalbard)

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Abstract: The paper presents changes in concentration levels of dioxin-like compounds that can be observed over the course of four study seasons in water samples collected from the Arctic watershed of Svalbard. The conducted analysis involved anthropogenic and natural factors that may affect the concentration of PAHs in the study samples of water. An attempt is made to indicate the emission source of the compounds being deposited and to identify the extent to which the substances under analysis actually affect the Arctic ecosystems. Moreover, the work employs the following: diagnostic ratios PAHs, air masses backward trajectory analysis, Lidar observations and land relief analysis in order to provide a multi-level interpretation of the obtained data. Natural environment constitutes a complex system of subtle correlations that need to be perceived as a dynamic medium, in which multi-faceted processes take place.

Keywords: polycyclic aromatic hydrocarbon; volcanic eruptions; cross-border pollution; arctic watersheds; Svalbard

1. Introduction

The article pursues to tackle the subject of pollutants migration in the polar setting in recognition of the role of the Arctic in the natural environment, particularly in shaping the Earth's radiation budget, emitted surface radiation, thermal balance of the atmosphere and the surface of earth, as well as shaping the weather and climate in the context of global changes that are currently taking place [1]. Moreover, substances that enter the atmosphere as a result of volcanic eruptions, forest fires and anthropopressure tend to contribute both directly (toxic effect of compounds and their derivatives) and indirectly (induction of glaciers melting processes and release of pollutants from permafrost thawing) to the pollution of soil and water [2,3]. Furthermore, considerable parts of the European Arctic are found within the influence range of Iceland, which is particularly volcanically active. Due to its geological location, there are approximately 130 volcanoes at the edge of tectonic plates in Iceland. The following diagram shows selected volcanic activity in Iceland in the years 1700–2015 (Figure 1).

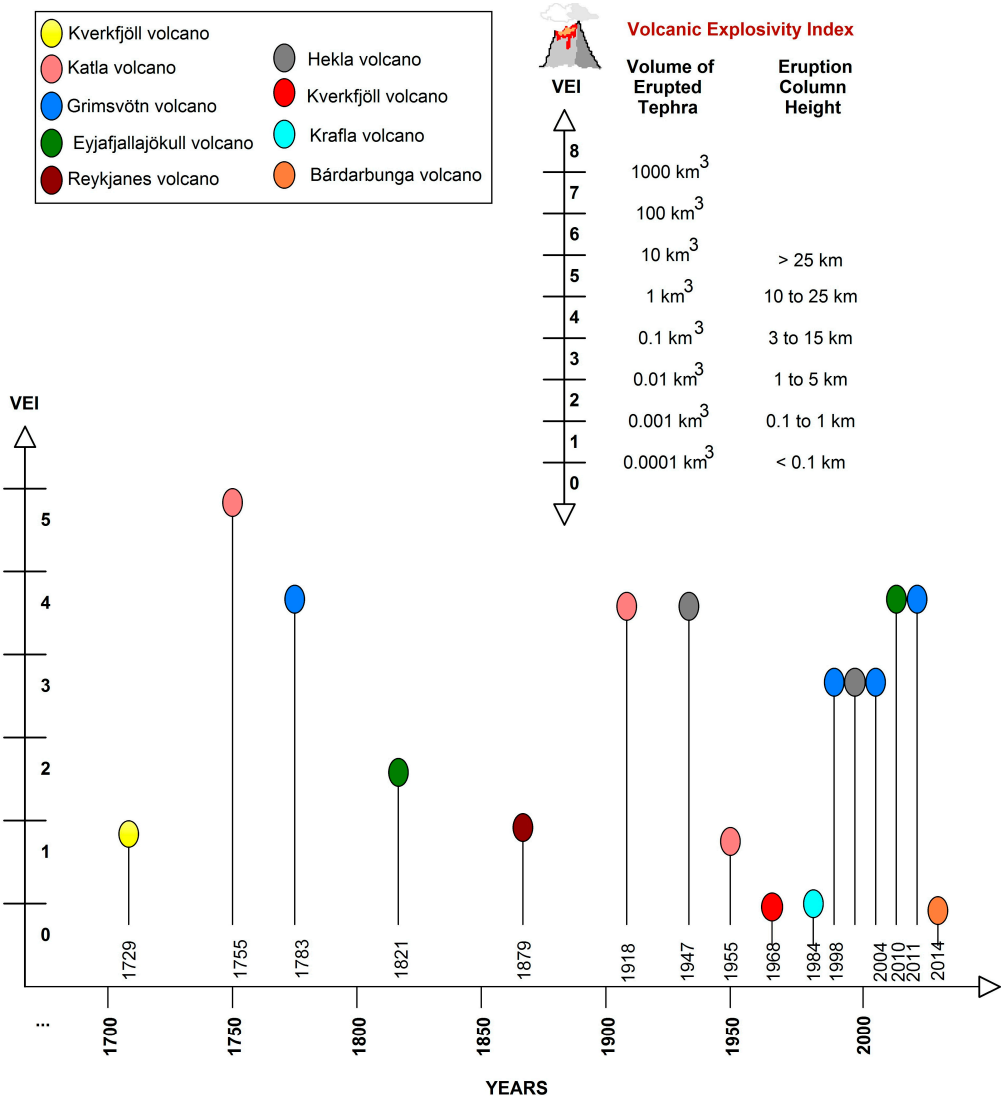

Figure 1. Selected volcanic activity of main volcanoes situated in Iceland.

Volcanic eruptions are regarded as one of the most intensive natural phenomena that involve emission of tons of pollutants into the atmosphere [4]. The intensity of eruption is described by the Volcanic Explosivity Index (VEI) which is based upon the volume of tephra produced during eruption. Due to the scale of this occurrence, some volcano eruptions constitute a particular threat to the areas of the Earth that are considered susceptible to changes [4,5]. Moreover, intensive eruptions that feature emission of dust and gases into the upper layers of the atmosphere not only contribute to the pollution of considerable parts of the Earth, but may also alter the characteristics of clouds, including polar stratospheric clouds, trigger the greenhouse effect, as well as introduce climate changes and their effects [6].

When analysing the available data on the impact of volcano eruptions on the environment, one may encounter numerous studies discussing the influence of volcanic eruptions on the atmosphere chemistry [3,5–9]. A number of interesting works has been published over the last decade, focusing on the impact of a spectrum of volcano-induced pollutants on the environment [10–12]. Despite the fact that there have been several papers touching upon the impact of volcano eruptions in the context of climate changes [3,8,13], there are large gaps in knowledge related to the influence of the Earth's internal geological activity in the global scale—in terms of organic compounds emission. It is thus of importance to attempt to estimate the impact of volcano eruption and the consequent release of

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compounds on remote areas, including particularly sensitive polar ecosystems. Nevertheless, it would be negligent if the authors were to ignore other potential sources of pollutants emission, including natural ones (e.g., fires of forests, grasslands, heathlands, and steppes), as well as anthropogenic emissions. It should be noted that in the unique environmental and geographical conditions, all of the listed emission sources may co-occur, strengthening the impact and compensating the adverse effects substances may have on the environment. The scholars investigating these aspects indicate, however, that there appears to be a "research gap" in terms of knowledge of emission of dioxin-like compounds from volcanic sources [14]. Svalbard area is rich in minerals, for example coal. There is a chance that some of PAHs emissions come from the mining but this source is local rather than regional. On a specific area of Fuglebekken catchment there are no significant sources of this mineral. The mountain ranges play a key role in the process of wet and dry deposition. The small mine in Longyearbyen can be omitted because it is only local and it cannot contaminate the Hornsund area. Hornsund fjord is located approximately 100 km at south of the main mine on Spitsbergen (Svaegruva). It is separated by the mountain area of Lands of Wedel-Jarlsberg and Torrell, which are well covered with glaciers with altitudes that (like relative) exceed 1000 m. This creates a barrier to the transport of pollutants from the mine. This is clearly visible in the parent atmospheric circulation. In the years 1951–2004, from the north only a few percent of air masses (<11%) were blowing compared to other directions [15]. Another thing is that the shape of the Bellsund fjord coast at the end of which the mine is located (Sveagruva) favors the wind blowing towards the east (whereas Hornsund fjord is located in the south). Similarly, the case of Ny-Ålesund's abandoned mine. In addition, the vast Isfjord and Adventfjord are conducive of blowing impurities in the east and northeast. The fact that the snow pollution by coal dust coming from the mines in Longyearbyen and Sveagruva is local, is well described in work Aammaas et al. [16]. To similar conclusions, concerning the concentration of PAHs in the local pollution in water of lakes near the abandoned mine in Ny-Ålesund came Jiao et al. [17]. Similar conclusions had Rose et al. [18] in their work, and on the basis of PAHs, PCBs in waters of the lake says that the burning of fossil fuels is local on Spitsbergen. In places outside the main areas of burning, more important is the deposition of material from long-range transport [18].

The presented work pursues to indicate the likely sources of emission of stable organic compounds falling into the dioxin-like group that have been detected and identified in the Arctic tundra environment, as well as to confirm the hypothesis concerning the impact of the Eyjafjallajökull volcano eruption (Iceland, 63.63° N, 19.62° W), from 14 April to 22 May 2010, and the relatively short eruption of the Grímsvötn volcano and the pollutants emission resulting from these occurrences on changes in the Arctic ecosystem of the southern part of the West Spitsbergen island (Hornsund fjord, Svalbard, 77.00° N, 15.33° E). Particular attention is given to polycyclic aromatic hydrocarbon compounds (PAHs) due to their documented harmful effect on the flora and fauna species of the Arctic [1,18,19]. PAHs tend to enter the aquatic environment mainly from the atmosphere (through dry deposition and precipitation) and in consequence of washing out polluted soil [20–22].

2. Materials and Methods

2.1. Sampling

Surface water from the main stream was collected in the Fuglebekken catchment at Hornsund fjord (sampling locations are shown in Figure 2). The water samples (N = 15, 1 L-volume) were collected in the summer session (25 June–9 July) every year from 2010 to 2013 (in total there were 60 samples).

Surface water samples were collected manually and stored in airtight bottles, triple rinsed with the sample water prior to its collection. This was performed with the bottleneck directed towards the water current to prevent the inflow of suspended contaminants. To avoid the post-sampling chemical composition changes, all material collected was stored and transported to the laboratory in airtight, dark, bottles, in cold storage (approximately +4 °C). A thorough pre-cleaning procedure was employed,

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with Neodisher LaboClean LA (an alkaline cleaning powder), a sequence of solvents and deionised water rinses deactivated the inside of the sampling containers, resulting in negligible losses of PHA by adsorption. The efficiency of the preparation procedures and good preservation of samples in transport was confirmed by validation tests on solutions of 20 ng·L^{-1} concentration of the PHA tested in this study (reproducibility and recovery from the standards were high (85%–95%)).

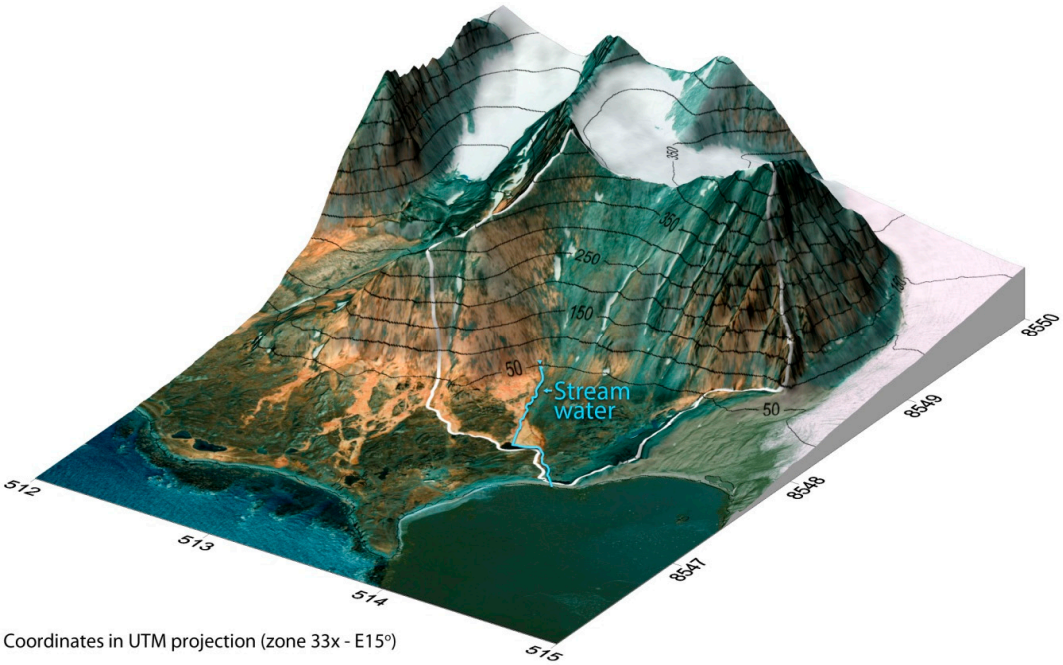

Figure 2. The sampling area location at Hornsund fjord, Spitsbergen.

The field studies did not involve endangered or protected species. The study was approved by the Norwegian Government's representative in Svalbard Norway.

2.2. Materialas and Analytical Procedure

All solvents used for sample processing and analyses were GC-pure quality and were purchased from the Sigma-Aldrich Company (dichlorromethane-PPESTANAL®, solvent for residue analysis; methanol-CHROMASOLV®, Saint Louis, MO, USA). A mixture of 16 PAHs and two deuterated internal standards (naphtthalene-d8, benzo(a)antthracene-d12) in dichloromethane at a concentration of 2000 µg/mL were from Restek Corporation (Bellefonte, PA, USA) and Supelco (Bellefonte, PA, USA) respectively. Milli-Q deionised water was used during the determination of the various target analyte groups.

A 500 mL sample of water was extracted with 15 mL dichloromethane, two deuterated internal standards (20 µL at a concentration of 2 µg/mL) (naphthalene-d8 (m/z 136) and benzo(a)anthhracene-d12 (m/z 240)), and shaken for 20–30 min. After the first extraction step the organic phase collected and proceeded to the next extraction stage by adding a further portion of solvent 15 mL of dichloromethane to the sample and shaking for 20–30 min. After liquid-liquid extraction (LLE), the two extracts were combined and evaporated to a volume of 300 µL under a gentle stream of nitrogen (Figure 3) [23–27].

The final extracts were analysed using an Agilent Technologies 7890A gas chromatograph with an Agilent Technologies 5975C mass spectrometric detector and splitless injector (7683B). A ZB-5MS capillary column (5% phenyl + 95% dimethylpolysiloxane, 30 m × 0.25 mm × 0.25 µm) was used. The temperature programme was the following: initial temperature 40 °C, 40 °C to 120 °C at 40 °C·min^{-1}, then 120 °C up to 280 °C at 5 °C·min^{-1} where it was held for 17 min. The carrier gas was helium with inlet pressure 70 kPa. The injection volume selected for all analyses was 2 µL.

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The mass spectrometer was operated in the selected ion monitoring (SIM) mode. The following ions were monitored: (m/z) PAHs: 128, 127, 152, 151, 154, 153, 166, 165, 178, 176, 203, 202, 228, 226, 252, 250, 277, 276, 279 and 278 [28]. Before the sample analysis, the relevant standards were analysed to check column performance, peak height and resolution, as well as the limits of detection and quantification. A solvent blank, a standard mixture and a procedural blank were run in each sequence of samples to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times.

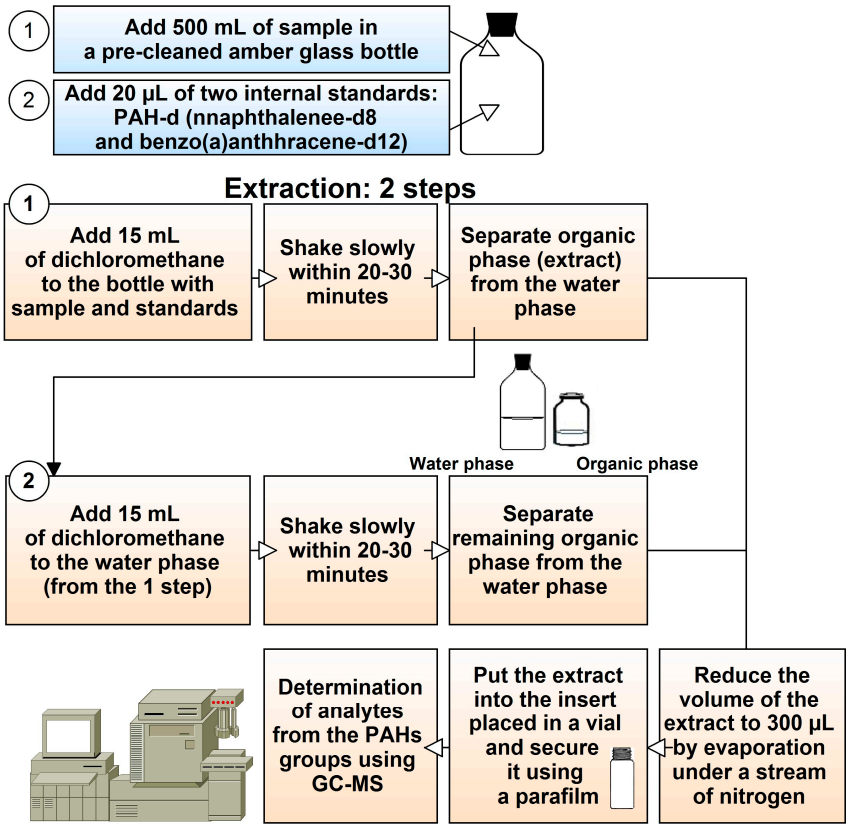

Figure 3. Scheme of extraction and preconcentration of surface water samples for determining PHA concentrations.

2.3. Quality Assurance/Quality Control (QA/QC)

All data were subject to strict QC procedures. The analytical procedures applied to the determination of individual components in environmental samples with various matrix compositions were validated against certified reference materials (QC1223 (low level PAHs in acetone); QC3308 (TOC in water matrix), Sigma-Aldrich Chemie Gmbh, Munich, Germany). The certified reference materials (CRM) were produced and certified in accordance with ISO Guide 34:2009 and ISO/IEC 17025:2005. All the obtained values for PAHs and TOC in CRM were in the interval of confidence. Reproducibility and recovery were high (85%–105%) with relative standard deviation (RSD) 4%–10%. Average recoveries of standards in the following validation studies were in range: 70%–85% and of internal standards 80% and 85% for naphthalene-d8 and benzo[a]anthracene-d12 respectively. Replicate samples and reference solutions were run after every five samples to assure the precision of each run. All blanks were analysed in the same setup as for the samples, using the same reagents. Technical specifications, reagents for determining selected parameters and analyte contents in samples, and basic validation parameters of the analytical procedures are summarized in Table 1.

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Table 1. Validation parameters, technical specifications and reagents used in the applied analytical procedures.

Analytical Techniques		Measurement Range	LOD	LOQ	CV (%)	Measurement Information	Reagents/Standards
NPOC *		0.15–10	0.030	0.10	0.1–1.5	**Total Organic Carbon Analyzer TOC-VCSH/CSN, SHIMADZU** (680 °C combustion catalytic oxidation/NDIR method)	Potassium Biphthalate, $C_6H_4(COOH)$ FW204.23, purity 99.9%, Kanto CO., INC., (Tokyo, Japan)
PAHs **	Naphthalene	1.02–3500	0.034	1.02	0.5–5	**Gas Chromatograph 7890A** (Agilent Technologies, Santa Clara, CA, USA) coupled with a mass spectrometer (5975C inert MSD—Agilent Technologies), detector (Agilent Technologies 5975C) with electron ionization (SIM mode)	Dichloromethane, Methanol Sigma-Aldrich Company; Naphthalene-d8, Benzo(a)anthracene-d12, Supelco; Mixtures of 16 PAHs (2000 µg/mL in dichloromethane), Restek Corporation
	Acenaphthylene	0.012–1000	0.004	0.012			
	Acenaphthene	0.012–1000	0.004	0.012			
	Fluorene	0.005–1000	0.002	0.005			
	Phenanthrene	0.008–1000	0.003	0.008			
	Anthracene	0.023–1000	0.008	0.023			
	Fluoranthene	0.042–1000	0.014	0.042			
	Pyrene	0.084–1000	0.028	0.084			
	Chrysene	0.007–1000	0.002	0.007			
	Benzo(b)fluoranthene	0.042–1000	0.014	0.042			
	Benzo(k)fluoranthene	0.007–1000	0.002	0.007			
	Benzo(a)pyrene	0.017–1000	0.006	0.017			
	Benzo(a)anthracene	0.005–1000	0.002	0.005			
	Benzo[g,h,i]perylene	0.004–1000	0.001	0.004			
	Indeno(1,2,3-cd)pyrene	1.29–1000	0.431	1.29			
	Dibenz(a,h)anthracene	0.042–1000	0.014	0.042			

Notes: * mg/L, ** ng/L, LOD—Limit of detection, LOQ—Limit of quantification, CV-Coefficient of variation, NDIR-Non-Dispersive Infra-Red detector.

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2.4. Factors for Results Analysis

2.4.1. Diagnostics Ratios

The sources of PAHs emission in water, soil and air were identified using diagnostic ratios (Table 2) [29,30].

Table 2. Selected PAHs diagnostic ratios.

PAHs Diagnostic Ratios	Potential Pollution Emission Sources	Reference
ANT/(ANT + PHE)	<0.1 Petrogenic >0.1 Pyrogenic	[31]
BaA/(BaA + CHR)	0.2–0.35 Coal combustion <0.2 Petrogenic >0.35 Pyrogenic	[32,33]
FLA/(FLA + PYR)	<0.4 Petrogenic 0.4–0.5 Fossil fuel combustion >0.5 Grass, wood, coal	[34]
IcdP/(IcdP + BghiP)	<0.2 Petrogenic 0.2–0.5 Petroleum combustion >0.5 Grass, wood and	[33]
(PHE/ANT)	>10 petrogenic origin <10 whereas combustion	[35]
(Fl/PYR)	≈1 indicate pyrolytic origins >1 attributed to petrogenic source	
BaP/BghiP	<0.6 Non-traffic emissions >0.6 Traffic emissions	[36]
FL/(FL + PYR)	<0.5 Petrol emissions >0.5 Diesel emissions	[29]

2.4.2. Impact of Volcanic Eruption

The obtained results were compared with the levels of dioxin-like compounds found in various types of materials formed during a volcano eruption (Table 3).

Table 3. Dioxin-like compounds in post-eruptive materials.

Post-Eruptive Material	Year and Place of Eruption	Dioxin-Like Compounds	Concentration/ Range	Reference
Muds pool	Vulcano Aeolian Island, the last eruption on the island occurred from 1888 to 1890 from the Gran Cratere.	NP; ACY; ACE; FL; PHE; ANT; FLA; PYR-1MET; PYR; BaA; CHR; BbF; BkF; BaP; PER; DahA; BghiP 1; IcdP	0.5–35.7 ng/g·dw	[37]
Gases and aerosols	Ashes erupted during period from 1975 to 1976 by the Tolbachik volcano, and 1983, 1985, and 1988 on the Mendeleev volcano, in a caldera of Golovnin volcano, and at the side crater of the Tyatya volcano formed during the eruption of 1973	Hydrocarbons, Aromatic polycyclic hydrocarbons	Identification	[38]
			Identification	[39]
Ash	The volcano Tjatja (Kunashir island, Kuriles) erupted in 1973	FLA; PYR; BaA; CHR; BbF; BkF; BaP; DahA	Identification	[40]
	From 20 July to 5 August 2001, a flank eruption with intense explosive activity occurred in Mount Etna.		0.16–11 ng/g	[41]

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2.4.3. Lidar Observations

The atmosphere constitutes a complex medium, which accommodates continuous reactions resulting in compound transformation (i.e., under the influence of photons, radicals), as well as processes of pollutant transport. Said processes depend on numerous climatic and meteorological factors, as well as the type of emission and physicochemical attributes of the substances being emitted into the atmosphere. The impact scale of an eruption can be verified against the height from which gases and dusts are ejected. Eruptions, in consequence of which material is thrown up to the height of the tropopause and stratosphere, are regarded as significant, as impact range of these occurrences goes beyond regional, continental and, in some instances, global boundaries [9].

Backward trajectory analysis provides information on the origin and source area of air masses. Moreover, the backward trajectory analysis method constitutes an excellent supplement to the use of synoptic maps, as it allows for indicating likely areas, where wet deposition may occur. LIDAR technology, on the other hand, allows for determining the vertical profile of backward dispersion coefficient for aerosol. The LIDAR method paired with air masses backward trajectory analysis allow for estimating the sources of aerosols and pollutant dispersion.

2.4.4. Differences in Deposition Impact between Research Stations

The location of the Polish Polar Station at Hornsund fjord may considerably affect the type and quantity of deposited pollutants. Therefore, the location of the Polish Polar Station has been presented in relation to two other stations (Zeppelin Mountain near Ny-Ålesund on Spitsbergen; station code: NO0042G); Andøya (continental Norway beyond polar circle; station code: NO0090R), which also conduct research on PAHs compounds (Figure 4). PAHs concentrations in air from Zeppelin Mountain and Andøya stations were used from EBAS data center operated by NILU and providing atmospheric composition data from international and national frameworks such as: European Monitoring and Evaluation Programme (EMEP), Arctic Monitoring and Assessment Programme (AMAP), Norwegian Institute of Air Research (NILU) and Comprehensive Atmospheric Monitoring Programme (CAMP).

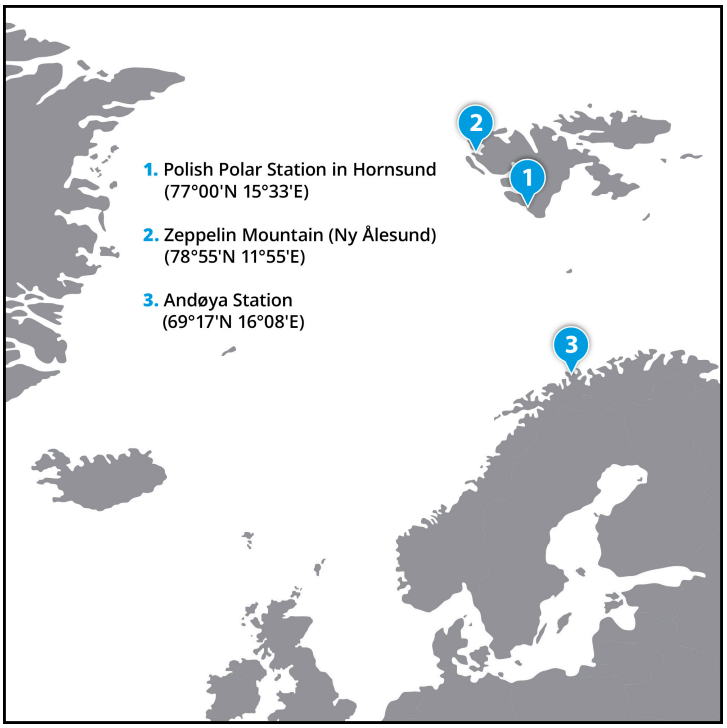

Figure 4. Location of the Polish Polar Station at Hornsund fjord in relation to other stations conducting research on PAHs compounds.

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The results were interpreted based on daily types of atmospheric circulation over Spitsbergen in the period of documented volcanic eruptions in Iceland. The authors conducted a spatial analysis of atmospheric pressure distribution with respect to possible pollutant migration, as well as examined the direction of air masses inflow.

2.4.5. Principal Component Analysis (PCA)

Principal component analysis (PCA) were performed on PAHs concentration in main stream draining Fuglebekken catchment using Statistica 12.5 to determine inter-correlation (internal relations) between PAHs for two periods: with volcanic eruption 2010–2011, and without volcanic eruptions 2012–2013. In total eleven valid PAHs concentration (ACY, ACE, FL, PHE, ANT, FLA, PYR, BaA, IcdP, DahA) were used in PCA analysis. PCA changes correlated data into uncorrelated principal components (PC) that are ordered by decreasing variance. Each of PAHs is correlated with each PC that is called factor loadings. As an input for PCA analyses we used correlation matrix based on standardized PAHs concentration. During PCA analysis for 2010–2011 period one outlier (sample from 8 February 2010) affected inter-correlation between PAHs and was omitted in further analysis.

3. Results

The paper presents the results of analyses conducted to determine the concentration of individual PAH compounds (NP; ACY; ACE; FL; PHE; ANT; FLA; PYR; BaA; CHR; BbF; BkF; BjF; BaP; BeP; DahA; BghiP 1; IcdP, as well as the following summary parameters: NPOC and $\sum_{16}$PAHs (Table 4).

3.1. Results Interpretation against Additional Factors

3.1.1. Diagnostics Ratios

The study results were analysed with the use of PAHs diagnostic ratios. The Table 5 shows PAHs diagnostic ratios calculated for the water samples collected from the Fuglebekken catchment area and offers comparison of selected attributes identified in 2009 and provided in the study by Polkowska (2011) [27].

The analysis of results revealed that there are several potential sources of PAHs emission in each of the analysed cases, which has been confirmed with the analysis of PAHs percentage concentration profiles. When comparing coefficient ratios, one may assume that in the years 2010 and 2011 the most likely source of PAHs emission were both potential source being petrogenic and pyrogenic. It should be noted that no coefficient can unequivocally verify natural sources of PAHs emission into the environment. Moreover, temperature differences that occur during a volcano eruption may significantly affect the composition of PAHs [42]. In their work, Zolotov and Shock described this particular aspect in detail as potential synthesis of condensed hydrocarbons during cooling and dilution of volcanic gases [42]. Taking into consideration similarities in terms of thermodynamics between the process of combustion and volcanic eruption, one can assume that the volcanic source of PAHs emission can be regarded as combustion. In the years 2012 and 2013, on the other hand, there was a notable increase in the coefficients that would indicate the source of PAHs emission as petrogenic, which can be related to human activity and ongoing anthropopressure in the Arctic region (long range atmospheric transport).

Comparing selected PAHs diagnostic ratios evaluated in water samples collected from the Fuglebekken catchment in the years 2010–2013 with those described by Polkowska in 2009 [28], an observation can be made that some of them originate from the same source. For instance, ANT/(ANT + PHE) in both studies are revealed to originate from pyrogenic sources. There are also some PAHs diagnostic ratios that differ one from another, for example FL/(FL + PYR) or (Fl/PYR). In Polkowska's work this compounds originate from petrol emissions and pyrolitic sources respectively. In this work, they come from diesel emissions and are of petrogenic origins.

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Table 4. Minimum, maximum, median and mean concentrations (ng/L) of different compounds determined in Fuglebekken catchment.

Name of the Compound Belonging to the PAHs Group	Abbreviation of the Compound Name	Number of Rings in the Aromatic Compound	2010				2011				2012				2013			
			Min	Max	Average N = 15	Median	Min	Max	Average N = 15	Median	Min	Max	Average N = 15	Median	Min	Max	Average N = 15	Median
Naphthalene	NP	2	177	5948	3090	3348	<LOD	82.5	9.04	<LOD	2.65	41.5	12.6	8.28	11.9	85.6	29.3	26.3
Acenaphthylene	ACY	3	<LOD	257	50.0	22.5	<LOD	65.5	10.6	2.56	3.19	63.5	20.8	15.1	5.60	96.3	33.4	24.6
Acenaphthene	ACE	3	<LOD	538	83.3	37.1	<LOD	8.73	1.43	0.74	<LOD	5.30	2.46	2.63	<LOD	36.6	10.8	9.47
Fluorene	FL	3	8.39	298	56.2	27.2	<LOD	<LOD	<LOD	<LOD	<LOD	6.98	1.96	1.30	<LOD	33.7	15.2	13.7
Phenanthrene	PHE	3	42.4	541	258	238	<LOD	3.29	0.51	<LOD	<LOD	57.8	15.2	15.0	<LOD	86.1	30.0	26.5
Anthracene	ANT	3	6.40	1143	106	15.0	<LOD	3.67	0.59	<LOD	<LOD	3.19	0.170	<LOD	<LOD	15.8	2.76	<LOD
Fluoranthene	FLA	4	7.63	656	72.7	16.2	<LOD	8.98	3.27	<LOD	<LOD	3.00	0.190	<LOD	<LOD	9.13	2.26	1.68
Pyrene	PYR	4	6.20	153	37.4	25.7	<LOD	38.3	2.55	<LOD	<LOD	5.62	0.510	<LOD	<LOD	80.6	10.7	<LOD
Benzo[a]anthracene	BaA	4	1.16	45.5	10.0	3.78	<LOD	55.9	11.3	6.39	<LOD	1.90	0.210	<LOD	<LOD	<LOD	<LOD	<LOD
Chrysene	CHR	4	<LOD	77.3	10.4	<LOD	<LOD	68.5	13.8	0.14	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo[b]fluoranthene	BbF	5	4.07	43.9	20.4	17.7	<LOD	0.650	0.14	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo[k]fluoranthene	BkF	5	<LOD	53.8	6.86	<LOD	0.230	116	20.1	10.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo[a]pyrene	BaP	5	1.10	35.1	8.35	4.12	3.40	2987	463	32.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Dibenzo[a,h]anthracene	DahA	5	<LOD	20.0	8.14	8.09	<LOD	244	87.4	93.1	<LOD	1.89	0.150	<LOD	<LOD	10.4	0.690	<LOD
Benzo[g,h,i]perylene	BghiP 1	6	<LOD	95.0	9.42	2.41	12.6	2361	626	744	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Indeno[1,2,3-c,d]pyrene	IcdP	6	<LOD	23.6	10.4	10.8	0.18	536	78.7	23.1	<LOD	6.54	1.00	<LOD	<LOD	<LOD	<LOD	<LOD
	$\sum_{16}$PAHs		695	6797	3838	3752	101	3477	1329	1278	13.3	104	55.3	48.0	59.7	332	135	110
	NPOC [mg/L]		1.28	2.97	1.94	1.83	1.13	4.54	2.27	2.17	0.42	1.82	1.08	1.05	0.50	1.95	1.32	1.20

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Table 5. Selected PAHs diagnostic ratios identified in water samples collected from the Fuglebekken catchment as compared to findings in literature.

PAHs Diagnostic Ratios	Potential Pollution	Lack of Volcanic Activity	Episodes of Volcano Erruptions		Lack of Volcanic Activity	
		2009 *	2010	2011	2012	2013
ANT/(ANT + PHE)	<0.1 Petrogenic		**0.011**			0.079
	>0.1 Pyrogenic	0.851		**0.540**	0.291	
BaA/(BaA + CHR)	0.2–0.35 Coal combustion					-
	<0.2 Petrogenic					-
	>0.35 Pyrogenic		**1.00**	**0.450**	0.490	-
FLA/(FLA + PYR)	<0.4 Petrogenic					0.174
	0.4–0.5 Fossil fuel, combustion		**0.268**			
	>0.5 Grass, wood, coal			**0.562**	0.660	
IcdP/(IcdP + BghiP)	<0.2 Petrogenic			**0.112**		-
	0.2–0.5 Petroleum combustion					-
	>0.5 Grass, wood and combustion		**1.00**		0.525	-
(PHE/ANT)	>10 petrogenic origin	0.771	**88.5**			10.9
	<10 whereas combustion			**0.853**	2.43	
(Fl/PYR)	≈1 indicate pyrolytic origins	0.628		-		
	>1 attributed to petrogenic source		**3.87**	-	1.50	1.42
BaP/BghiP	<0.6 Non-traffic emissions				-	-
	>0.6 Traffic emissions		**0.886**	**0.740**	-	-
FL/(FL + PYR)	<0.5 Petrol emissions			-		
	>0.5 Diesel emissions	0.755	**0.601**	-	0.794	0.586

Note: * [27].

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Natural sources of PAHs emission are frequently treated as background and regarded as insignificant [43]. The authors of this paper agree with the opinion, albeit only when natural emission remains at negligible level. In the cases of intensive volcanic activity or large-scale forest fires, this factor cannot be ignored.

3.1.2. Impact of Volcano Eruption on the Occurrence of Dioxin-Like Compounds

Volcanic eruptions are not only a source of secondary emission of compounds, but also constitute the synthesis reaction chamber of numerous organic compounds (Table 3). The process of organic compound synthesis from dusts and gases of an eruption cloud is complex conditioned by a number of factors: dustlike particles of rocks, shock waves, electric discharges and high temperatures [36]. Volcano eruptions certainly play a significant role in global transport of organic compounds (including PAHs), and considerably impacted the process of chemical evolution and the formation of life in the past. Figure 5 shows diagrams prepared on the basis of the data found in Table 3 to offer comparison with the data compiled for the purpose of this study. The diagrams show the percentage content of individual PAHs (including the number of rings) against total PAHs mass identified in the samples found after the volcano eruption: mud [33] and ash [37].

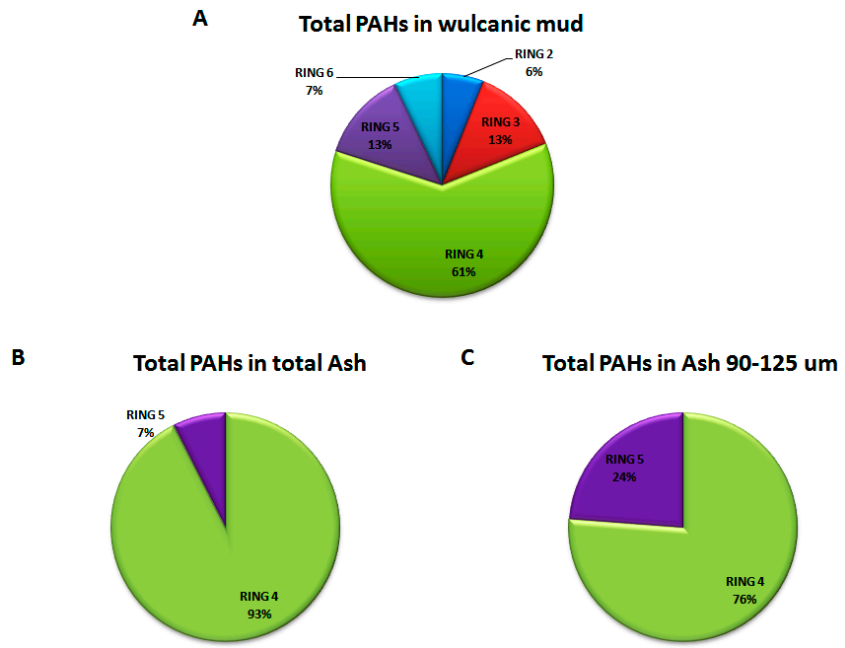

Figure 5. Percentage content of individual PAHs against total PAHs mass detected in the samples: A-mud [33]; B-total ash [37]; C-fraction of ash [37].

The analysis of the results obtained during the study indicates an abnormal increase in all PAHs found in the samples collected in the years 2010 and 2011. It is important to note that sample collection campaigns were preceded by two great volcano eruptions: the Eyjafjallajökull volcano (Iceland, 63.63° N, 19.62° W), from 14 April to 22 May 2010 [44] and relatively short eruption of the Grímsvötn volcano (Iceland, 64.42° N, 17.33° W), from 21 to 28 May 2011 [45]. Both eruptions emitted thousands of tons of pollution into the atmosphere, and the resulting volcanic dust clouds paralysed air transport for a long time [46,47]. It is highly probable that the pollutants in the eruption clouds were deposited in the region of the Arctic. The Polish Polar Research Station at Hornsund fjord (Spitsbergen, 77.00° N, 15.33° E), equipped with light detection and ranging system (LIDAR), registered changes in the atmosphere (aerosol, volcanic dust) at various altitudes, which emphasizes the scale of both eruptions [48]. Nevertheless, when discussing the process of pollution deposition in

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the specific components of the environment, one may not ignore the key role of meteorological factors (air temperature, air humidity and precipitation, atmospheric pressure, air movement, insolation).

Investigation of changes in the concentration of individual PAHs over the course of several years indicates the response of the environment to the occurrences that took place in that time. In 2010 and 2011, during the sample collection campaigns preceded by volcanic eruptions in Iceland, an increase was recorded in the concentration of $\sum_{16}$PAHs: 695–6797 ng/L and 101–3477 ng/L respectively. To put this in perspective, in the years 2009, 2012 and 2013, the concentration amounted to, respectively, 4.0–603 ng/L [27]; 13.3–104 ng/L; 59.7–332 ng/L. It can be thus observed that in 2012 concentrations of PAHs compounds were comparable to the level from the year 2009, i.e., prior to the volcanic eruptions (2010 and 2011), which were discussed in the work of Polkowska [27]. It is worth noting that in the years 2012–2013 the concentration levels of the most toxic compounds in the PAHs group (CHR; BbF; BkF; BaP; DahA; BghiP 1; Icd) were below the detection limit, whereas in the years 2010–2011, all the above-mentioned compounds were identified. Similar situation to PAHs may be observed in NPOC (non-purgeable organic carbon) concentration levels. In 2010 and 2011, NPOC concentration levels differed significantly from the others' findings and they were much higher than in the years 2012–2013. It is also connected with two huge volcanic eruptions in Iceland (Eyjafjallajökull and Grimsvötvn volcanoes). NPOC is also known as TOC (total organic carbon) and comprises a large range of compounds with a variety of properties. TOC is released to the environment from both natural and anthropogenic sources. Apart from volcanic eruptions, all aquatic organisms release TOC through their normal metabolism, excretion and eventual decomposition. Higher NPOC concentration levels in the collected samples may be a consequence of accumulation of all carbon compounds in the Arctic and increasingly frequent volcanic eruptions. In order to better determine the sources of PAHs emission, the results are presented in the form of percentage share of individual compounds with a given number of rings in the total number of PAHs (∑16PAHs) detected in the surface water samples collected in the Fuglebekken catchment area over the years 2010–2013 (Figure 6).

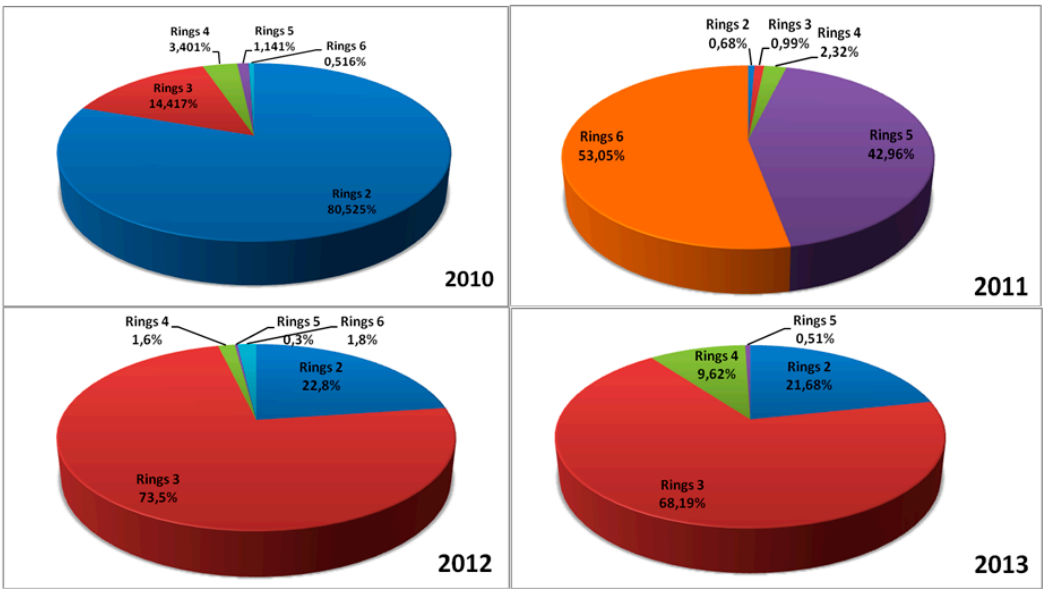

Figure 6. Percentage share of individual compounds with 2, 3, 4, 5 and 6 rings in total number of PAHs in the total number of PAHs (∑16PAHs) detected in the surface water samples collected in the Fuglebekken catchment over the years 2010–2013.

The results analysis is unfortunately very complicated, as other sources of PAHs can effectively increase concentrations of these compounds: forest fires, inflow of contaminated air masses from industrial areas, as well as possible local and regional emission sources, natural processes forming

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crude oil, bituminous shale and coal, synthesis by sea algae and biosynthesis by microorganisms [40] (Figure 7). Comparing the profiles of percentage content of PAHs (Figure 6) with the data presented in the work by Ravindra [29], one may conclude that other likely sources of PAHs emission included: coke ovens in 2010, diesel engines in 2011, and in the years 2012 and 2013—wood combustion. Detailed analysis of the data reveals a marked difference in the concentration of compounds with lower number of rings (2 and 3) between 2010 and the following years. Podkletnov and Markhinin (1981) [38] demonstrated that heating at 340–1000 °C a H_2O:CO_2:NH_3 mixture in the 90:90:1 v/v ratio (simulating the composition of volcanic gas) in a reactor containing volcanic ash, light PAHs (mainly 2–3 ring) are formed together with nitrogen containing organic compounds [38]. Furthermore, in 2011 a large concentration of compounds with high number of rings (5 and 6) was detected, which may have been a consequence of different composition of magma and different course of thermodynamic synthesis of PAHs from volcanic gases and dust, which considerably affects the chemistry of volcanic aerosols [40,42]. One should also take into consideration the impact of photochemical processes (on non-adsorbed PAHs), degradation during the hot season, as well as deposition of some hydrocarbons, all of which may affect the percentage content of individual PAHs [29,49]. On the other hand, the most important source of PAHs in the troposphere involves combustion processes, such as forest fires, power plants, incinerators, as well as diesel and gas engine exhausts [37]. The works of Culotta and Stracquadanio, who also touch upon the subject of organic compounds of vulcanic origin, indicate differences in PAHs composition in air, sediment and mud samples [37,41]. In his work, Stracquadanio places particular emphasis on the size of vulcanic dust fraction as a transport medium for individual PAHs compounds, hence identifying another factor that verifies deposition of post-eruption pollutants in the environment [37].

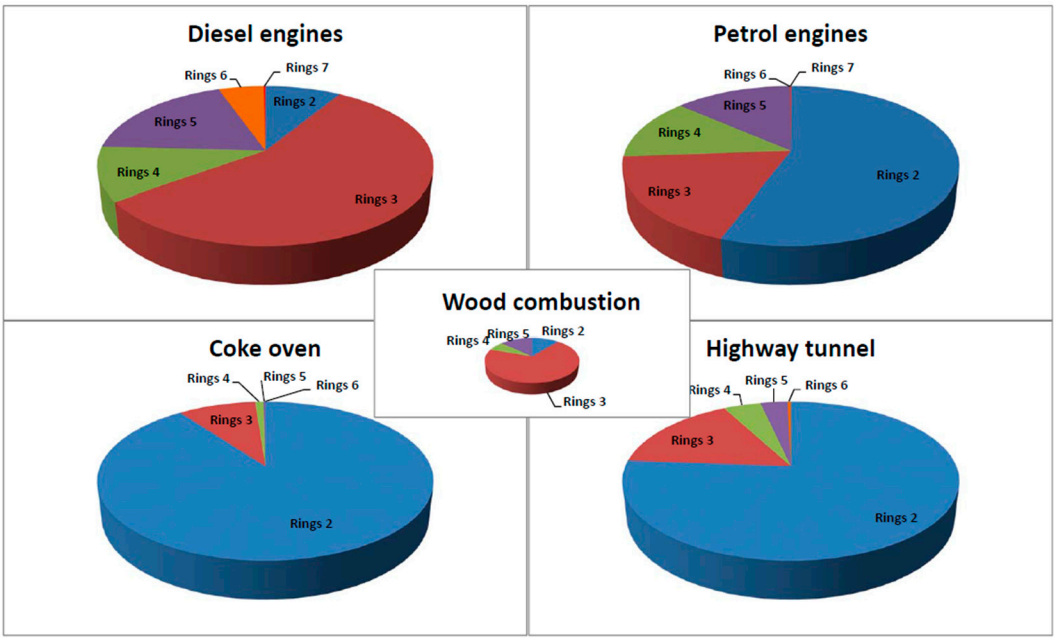

Figure 7. Source distribution of percentage PAHs to total mass [29] (total concentration of the measured 20 PAHs from highway tunnels, diesel engine, petrol engines, coke oven, and wood combustion in air samples, respectively).

In addition, PCA gives an insight into relationship between PAHs during periods with and without volcanic eruptions (Figure 8). In 2010–2011 principal components 1 and 2 (PC1 and PC2, respectively) explain 37.1% and 18.9% of total variance of all PAHs included in PCA, respectively. In 2012–2013, PC1 and PCA explain 34.4% and 19.1% of total variance of PAHs included in PCA, respectively. In 2010–2011, very strong inter-correlation between ANT, FLA, PYR and FL was observed.

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In 2012–2013 ANT and FLA had negligible inter-correlations with FL and PYR. During 2012–2013, NP and ACE had stronger correlation with PC1 than during 2010–2011. In addition, in 2010–2011 NP had no correlation with FL and PYR, whereas was strongly correlated in 2012–2013. FL, PHE and PYR were featured by similar correlation with PC1 in both periods. Thus, some of PAHs (ANT, FLA) are strongly associated with periods of volcanic eruption, whereas others (ACE, NP) are related to non-volcanic activity such as a long-range transport of contaminants in air. During both periods, correlations of FL, PHE and PYR with PC1 were similar that suggest these PAHs are not influenced by volcanic activity.

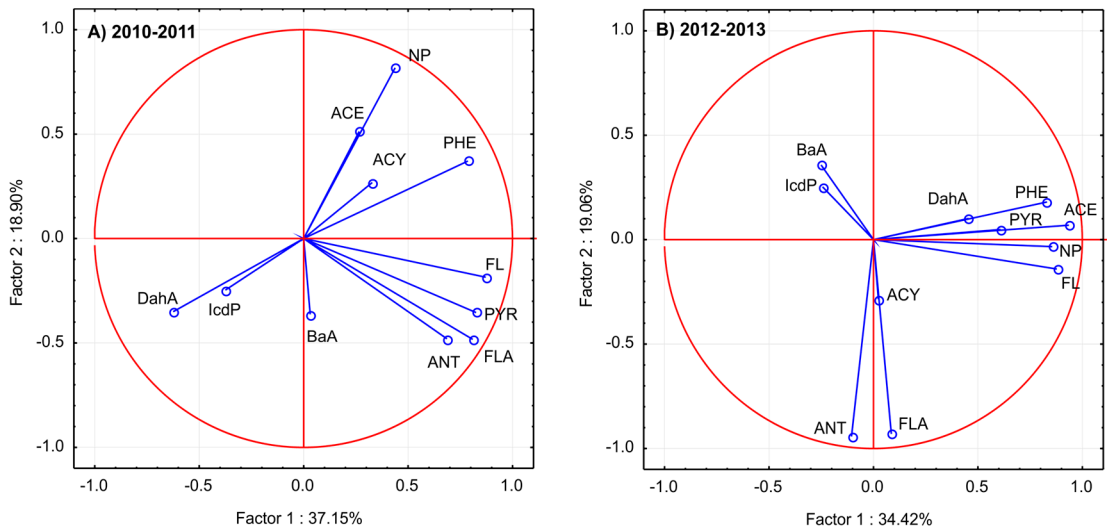

Figure 8. PCA of PAHs in the main stream in Fuglebekken catchment during period of: (**A**) volcanic eruptions 2010–2011; (**B**) without volcanic eruptions 2012–2013. PCA was calculated from the correlation matrix of the standardized concentrations of PAHs. Similar direction of line shows strong inter-correlation between concentrations of PAHs, whereas opposite shows strong negative correlation between concentrations of PAHs. Perpendicular directions of lines shows no inter-correlation.

It is note-worthy that in the years 2012 and 2013, composition of individual PAHs compounds display considerable similarities. Moreover, PAHs concentration levels are comparable to the results of research conducted in 2009 at the exact same location and using the same types of samples (of the same degree of matrix complexity), as well as identical final decantation method, as described by Polkowska [27]. Said similarity may indicate a lack of influencing factors outside those, which occur in the environment of this region—minimum human activity (potential local impact) and natural sources.

Backward air masses trajectories may considerably help in the analysis of pollutant deposition, and thus, in the attempt to answer the questions put forward.

3.1.3. Lidar Observations of Volcanic Dust over Polish Polar Station in Hornsund after Eruptions of Eyjafjallajökull and Grímsvötn

Observations of aerosol formed in the volcanic eruption, were conducted at the Polish Polar Station in Hornsund on 18 and 25 May 2010 (Eyjafjallajökull), and 25 May 2011 (Grímsvötn) [48]. In both said cases minor amounts of aerosol, in relatively thin layers (~200 m), were observed at an altitude of over 2 km, which precludes material deposition on the surface of Earth.

The analysis of backward air masses inflow trajectories at the time of volcanic eruptions in Iceland indicates two cases, when the air from the Eyjafjallajökull volcano appeared in the vicinity of the station in Hornsund, i.e., 21, 23 and 25 May 2010 (see Figure 9 for trajectories). Layers of volcanic aerosol could occur at an altitude of 1500–2000 m. In the case of the Grímsvötn volcano, computed backward trajectories allow stating that only on 3 June 2011 air came in from the volcano's region.

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On that day, volcanic aerosol clouds occurred at an altitude of 700 and 2000 m [48] (See Figure 10 for trajectories).

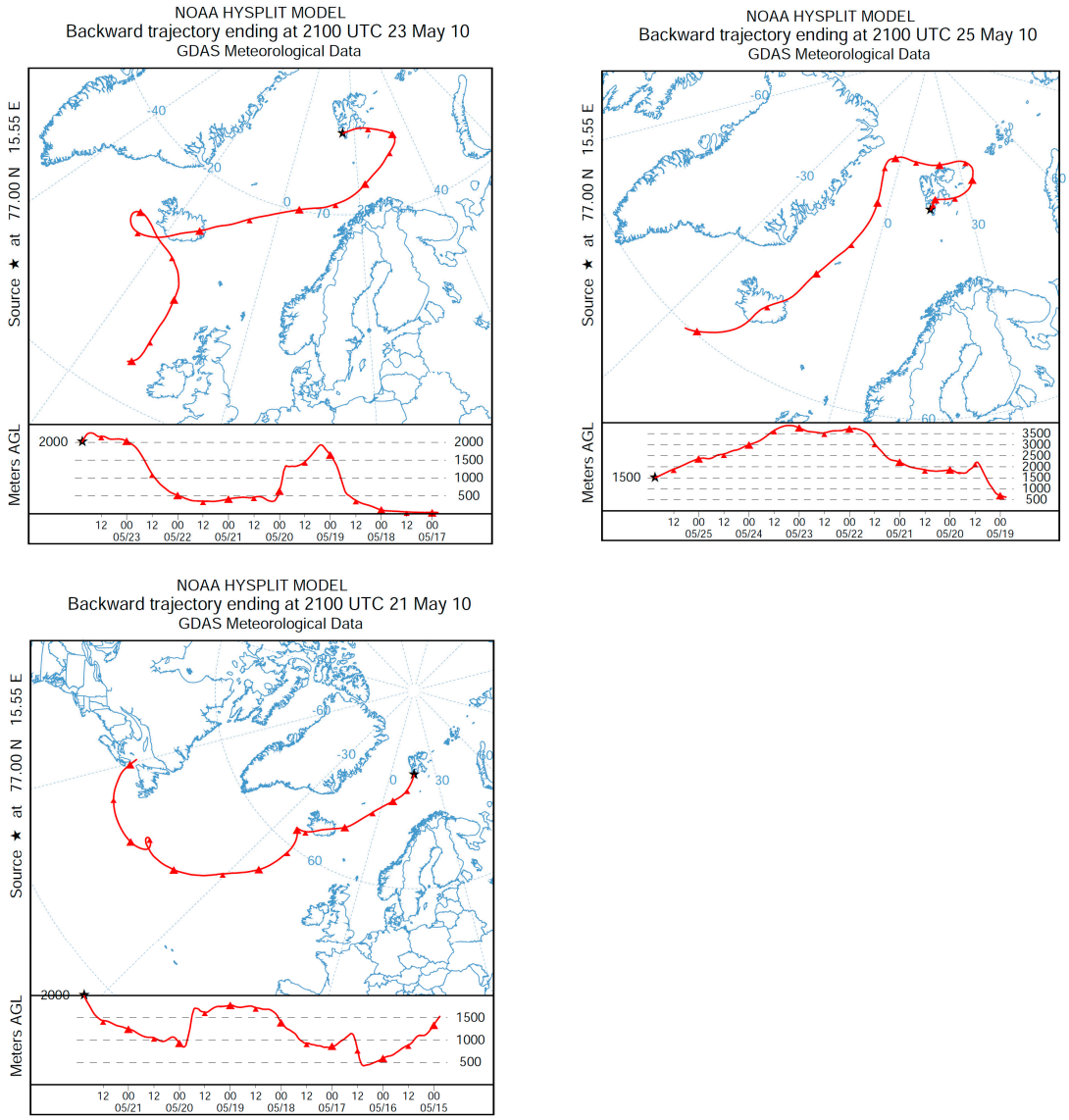

Figure 9. Trajectories of air masses inflow in the region of Polish Polar Station at Hornsund fjord during Eyjafjallajökull eruption in 2010.

Both LIDAR observations and trajectories analysis indicate only individual cases of volcanic aerosol being transported into the region of the Station in Hornsund. Each time the possibility of deposition was eliminated due to the considerable altitude of its occurrence or expected occurrence. Moreover, LIDAR observations and photometer measurements confirm that the amounts of transported material were small. These data do not allow for an unequivocal identification of increased PAHs concentrations with volcanic eruptions in Iceland of 2010 and 2011 (albeit it may not be ruled out). For determination of air masses backward trajectories, we used Air Resources Laboratory (ARL) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model [50]. As meteorological data for the model, Global Data Assimilation System (GDAS) [51], data were used. The data are provided by NOAA's (NAtional Oceanic and Atmospheric Administration (U.S. Department of Commerce) ARL.

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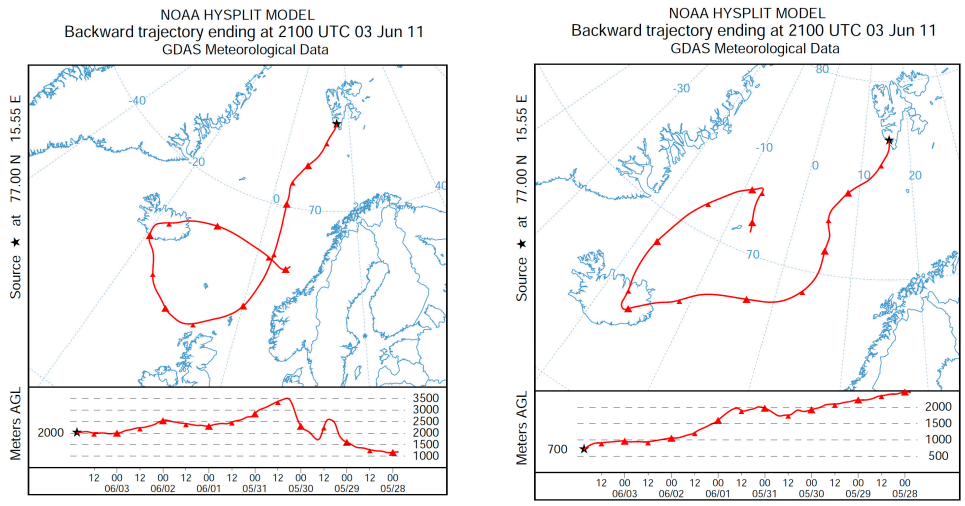

Figure 10. Trajectories of air masses inflow in the region of Polish Polar Station at Hornsund fjord during Grímsvötn eruption in 2011.

3.1.4. Analysis of Location Impact on Pollutant Deposition

In order to illustrate the influence of location on pollutant deposition in the area of the polar station in Hornsund, an analysis has been prepared concerning the concentrations of PAHs in the atmospheric air examined at the Zeppelin Mountain (Ny-Ålesund, Spitsbergen) and Andøya stations located in northern Norway, above the Arctic Circle (Table 6). Since there is a lack of PAHs measurement of air at Hornsund station, we assume that arrival of PAHs with air masses was ca. half day before reaching Ny-Ålesund (Figures 8 and 9). Thus, PAHs concentration of air in Hornsund shown in Table 6 is similar to Ny-Ålesund.

Table 6. Average concentration and standard deviation of selected PAHs (ng·m^{-3}) in the atmospheric air collected once a week from the stations included in EBAS Data Centre (NO0042G Zeppelin Mountain (Ny-Ålesund) and NO0090R Andøya) before, during and after the Eyjafjallajökull eruption in 2010 (based upon data available on EBAS Data Centre[52]).

PAHs in 2010	Before Eruption 15.02–7.04 (N = 8)	During Eruption 12.04–21.05 (N = 7)	After Eruption 24.05–28.07 (N = 10)	Before Eruption 10.02–8.04 (N = 8)	During Eruption 14.04–20.05 (N = 5)	After Eruption 26.05–29.07 (N = 8)
	Ny-Ålesund			Andøya		
Acenaphthene						
Average	0.030	0.030	0.030	0.058	0.058	0.058
StdDev	0.001	0.001	0.001	0.006	0.001	0.003
Acenaphthylene						
Average	0.005	0.004	0.003	0.011	0.019	0.006
StdDev	0.005	0.003	0.001	0.008	0.032	0.002
Benzo_a_fluoranthene						
Average	0.002	0.001	0.001	0.004	0.001	0.001
StdDev	0.004	<0.0003	<0.0003	0.006	<0.001	<0.001
Benzo_ghi_perylene						
Average	0.010	0.002	0.003	0.013	0.005	0.004
StdDev	0.016	<0.0003	0.001	0.016	0.002	<0.001
Inden_123cd_pyrene						
Average	0.010	0.001	0.001	0.011	0.002	0.002
StdDev	0.021	0.001	<0.001	0.016	0.001	0.001
Naphthalene						
Average	0.761	0.132	0.091	0.264	0.255	0.130
StdDev	0.294	0.095	0.019	0.131	0.281	0.008

Notes: * During these periods, concentrations of Benzo_a_fluoranthene and Benzo_ghi_perylene provided by EBAS Data Centre were equal. Therefore, we omitted calculations of standard deviations (StdDev).

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PAHs deposition in the catchment areas located at the Hornsund fiord (southern Spitsbergen) is facilitated due to land relief of this part of the Island. The fiord is blocked off from the north, south and east with high mountain ranges and glaciers. The highest peak in the area is the alpine Hornsundtind mountain—1431 m.a.s.l. [53]. Moreover, the Hornsund fiord is well exposed and, at appropriate atmospheric pressure, is subject to the inflow of air masses from Iceland (low pressure area over Spitsbergen and high-pressure area over Iceland) [54]. In the period of the volcanic eruption, i.e., from 14 April to the end of September 2010, air masses inflow in the Hornsund region from the west and south-west sector occurred over the course of 22 days, whereas in 2011, from 21 May to 30 September, such pressure system were observed 14 times [55]. Lack of notable change in the analysed chemical compounds at the Ny-Ålesund station (in relation to the situation from before and after the volcano eruption) is likely a result of unfavourable lie of the land (land surface featuring minor elevation differences), whereas in the case of the Andøya station (north Norway) it may be a consequence of air masses trajectory bypassing the area in question.

4. Summary

Rapidly growing human population and technological development exert great pressure on the environment. Progressing anthropopressure paired with a lack of understanding for the complexity and the nature of phenomena occurring in the biosphere frequently exceed the natural buffer capacity of the environment and, in consequence, generates numerous environmental problems. The results of research show that surface waters of the Arctic are markedly polluted with the PAHs compounds. During the four year-long campaign, preceded by volcanic eruptions in Iceland of 2010 and 2011, an increase was recorded in the concentration of $\sum_{16}$PAHs: 695–6797 ng/L and 101–3477 ng/L respectively. In contrast, in the years 2009, 2012 and 2013, the concentration levels amounted to, respectively, 4.0–603 ng/L [27]; 13.3–104 ng/L; 59.7–332 ng/L.

Based on the collected data an attempt was made to indicate likely sources of these compounds. It is of utmost importance to differentiate between the natural and anthropogenic sources of contaminants. Only by learning more about the natural changes and circulation of given components in the environment is it possible to assess the anthropogenic impact, and only then will it be possible to introduce well-defined and effective environmental recovery programs and legal regulations.

The work pursued to investigate and analyse the sources of dioxin-like compounds emission. The results do not allow for an unequivocal conclusion that the increased PAHs concentrations were caused by volcanic eruptions, as there were other likely sources of these compounds, and the influence of this cannot be neglected: coke ovens in 2010, diesel engines in 2011, and in the years 2012 and 2013—wood combustion. Nevertheless, the authors of this work disagree with the claim that natural sources of emission are negligible in comparison to anthropogenic emissions.

As we face the shifting climatic and environmental conditions and extreme phenomena, a great urgency arises to investigate the relationship between the polar regions and other parts of the Earth. Arctic environment constitutes a complex system of subtle correlations, which can be perceived as a dynamic medium for multi-faceted processes that may affect the entire planet. Human impact and extreme natural occurrences affecting even a single environmental component or element may entail far-reaching consequences and cause changes even in the most remote areas, including the polar region.

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concentrations in atmospheric air (Acenaphthene, Acenaphthylene, Benzo_a_fluoranthene, Benzo_ghi_perylene, Inden_123cd_pyrene and Naphthalene), which are available on EBAS Data Centre webpage (http://ebas.nilu.no), from Zeppelin Mountain (Ny-Ålesund, Spitsbergen) and Andøya stations.

Author Contributions: Katarzyna Kozak designed the concept, designed the experiment, prepared chemical properties analyses, analysed and interpreted the data, prepared figures, prepared and reviewed the manuscript; Marek Ruman selected the study area, supervised data collection, analysed environmental conditions and geographical factors, helped with gathering field data, prepared figures, reviewed the final manuscript; Klaudia Kosek interpreted obtained results, prepared figures, prepared and reviewed the manuscript; Grzegorz Karasiński interpreted the results and prepared the manuscript, prepared figures; Łukasz Stachnik helped with gathering field data, supervised data collection, prepared figures, prepared and reviewed the manuscript; Żaneta Polkowska provided support and guidance throughout the field experiment, analysed and interpreted the data, wrote the draft of the manuscript, reviewed the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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